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天然水体的镉/铜络合容量的动力学分析方法的研究

CdCC/CuCC in Natural Waters Evaluated by Dynamic Analytical Methods

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摘　要

水体中重金属元素的毒性和生物可利用性与其存在的形态有关。由于天然水中存在富里酸和腐殖酸等有机配体，它们能与游离态的重金属离子形成配合物，使其变成络合态，从而降低了重金属离子的危害性。天然水中的配体控制着重金属离子的存在形态，天然水中有机物对重金属离子的这种容纳能力可用络合容量(Complexing Capacity，CC)，即能与重金属离子形成配合物的有机物的总量来表示。研究天然水体对重金属离子的络合容量，可以了解水体对重金属的自净能力，不仅对于研究重金属污染物在水体中的迁移、转化具有一定意义，而且对于水质标准的确立和重金属污染风险评价也可提供科学依据。

测定水体中重金属元素 CC 的方法主要有电化学法、树脂交换法和溶剂萃取法。其中电化学法包括阳极溶出伏安法（ASV）和阴极溶出伏安法（CSV），溶剂萃取包括反萃法和液-液萃取动力学法。电化学法、树脂交换法和溶剂萃取的反萃法从测定原理上来说均属于以热力学平衡为基础的分析方法。相对而言，液-液萃取动力学方法是以动力学为理论基础的分析方法，不但可以测定重金属离子的络合容量而且可以同时给出相应配合物的易变性常数。

本文采用双硫腙、二（1，1，3，3-四甲基）丁基单硫代膦酸（HMTP）、螯合树脂作为水体中金属配合物的竞争配体，分别研究了天然水体当中的镉，铜络合容量（CdCC，CuCC）及对应金属配合物的易变性常数，并结合水体中的 C、S、N 等元素浓度的分析，探讨其络合容量的变化规律。全文包括以下几个部分：

第一章主要对重金属镉、铜的危害以及络合容量的研究进展进行了综述，阐述重金属对人体的危害，以及镉、铜污染的来源，介绍了络合容量的概念，阐述了络合容量对重金属形态研究的意义，对络合容量的研究方法进行了详细的介绍，并提出用各种不同的动力学方法研究天然水体对重金属的络合容量的设想。

第二章以双硫腙为萃取剂，在前人工作的基础上，考察双硫腙萃取剂对 Cd 配合物的萃取过程中动力学行为。首先用柠檬酸钠、NTA、HEDTA、EDTA 等模拟配体来检验方法的可行性，然后将该方法应用于闽江水样的 CdCC 研究。并分析了闽江水样的 DOC、N、S 等含量，发现闽江水体中 CdCC 与 DOC 和 S 含量有显著的相关性。将该方法与阳极溶出伏安法（ASV）对天然水体和 NTA 模

拟水样做了对比实验，两种方法的结果较为接近，相对偏差小于 20%，双硫腙萃取动力学法测得的 CdCC 比 ASV 法略高。

第三章进一步调整作为竞争配体的萃取剂的萃取能力，选择萃取能力适中的 HMTP 作为萃取剂，优化实验条件建立了新的萃取体系的动力学模型。通过模拟配体实验的检验，将该方法应用于闽江水样 CuCC 和 CdCC 的分析。发现测得的闽江水样的金属配合物存在两种不同形态，即易变形态和稳定形态，易变性常数分别表示为 k_{obsd1} 和 k_{obsd2}。结合水样的 DOC、N、S 浓度分析，发现闽江水体中 CdCC 与 DOC 和 S 含量有显著的相关性，而与 N 含量无明显的相关性；CuCC 与 DOC 和 N 存在显著的相关性，而与 S 含量无明显的相关性，这符合软硬酸碱理论的规律。将该方法与双硫腙萃取动力学法和 ASV 法进行了对比，发现对于同一水体，测得的金属络合容量较为接近，相对偏差小于 20%。其中 HMTP 萃取动力学法测得的 CC 略高于双硫腙萃取动力学法，双硫腙法略高于 ASV 法。

第四章尝试用螯合树脂代替有机萃取剂，通过实验条件的优化，建立了树脂交换反应体系的动力学模型，使之适合于天然水体 CdCC 的分析。先用模拟配体进行了模拟实验，对于像 EDTA 这种强配体，可以测出其 CdCC，测得的镉配合物易变性常数趋近于零；对于像柠檬酸这类弱的有机物配体测得的 CdCC 偏低；而对于像腐殖酸、NTA 的中等强度的有机配体，可以得到良好的结果，既可以测得其络合容量，又可以测得对应镉配合物的易变性常数，所以该方法可用于天然水体的络合容量研究。将该方法应用于厦门大学化学湖和芙蓉湖的实际水样测定，并与 HMTP 萃取动力学法做了比较，相对偏差小于 7%，证明该方法可应用于实际水样测定，相对于液-液有萃取动力学法，进一步简化了实验流程，有利于实现在线检测。

第五章总结了本硕士论文的研究工作，对其不足进行了检讨，并对将来进一步研究工作进行了展望。

关键词：金属络合容量；动力学法；易变性常数；天然水

Abstract

The toxicity and/or bioavailability of heavy metals in natural waters depend on their chemical forms. Since there are ligands such as humic acid and fulvic acid in natural waters, the toxicity and/or bioavailability of heavy metals would be reduced by forming complexes via the coordination of ligands to the metals. On the other hand, a speciation analysis of a water sample is necessary for understanding the toxicity, bioavailability, bioaccumulation and transport of a particular element such as cadmium and copper. Under such a circumstance, the concept “Complexing Capacity” (CC) has been introduced. The characteristic of occurring ligands can be expressed with the CC which can be deemed to self-purification capacity of natural waters.

Up till now, various methods for the measurement of the CC have been reported such as anodic stripping voltammetric (ASV), ion exchange, ion selective electrode and back extraction based on the principle of thermodynamic equilibrium, while dynamics based methods using liquid-liquid extraction and chelating resin enable the simultaneous determination of the CC and the observed lability constants (k_{obsd}) of metal-complexes involved. In this thesis, diphenyl thiocarbazone (dithizone) and bis(1,1,3,3-tetramethylbutyl)monothiophosphinic acid (HMTP) as well as methylene monoamino diacetic acid chelating resin (MADA) was used to as competing ligands to study and determine Cd and Cu complexing capacities of natural waters and the corresponding Cd/Cu k_{obsd}. These strategies were applied to evaluate the self-purification capacity of natural waters and predicate the risk of heavy metal pollution in water system. This thesis consists of 5 chapters.

In Chapter One, the pollution and subsequent impacts on the environmental and biological systems of heavy metals such as Cd and Cu were briefly reviewed, and the concept of the CC and its significance for evaluating of the self-purification capacity of natural waters and the state of the art for determining the metal CC was introduced. The objectives of this thesis was thus proposed to establish dynamic methods for simultaneous determination of Cd/CuCC and k_{obsd} as well as the evaluation of the risk of heavy metal pollution.

In Chapter two, a theoretic model of the dynamic extraction using dithizone as an competing ligand was established for for determining CdCC and teh corresponding k_{obsd} of natural waters. The feasibility of the method was validated by using the mimic water samples containing some model chelating agents such as ethylenediaminetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylene-diamine-N,N′,N′-triacetic acid (HEDTA), nitrilotriacetic acid (NTA) and humic acid. The method was applied to the real water samples collected from different sites of the Minjiang River which locates in the southeastern China. The CdCC are from 7.20 to 7.78 μ mol L^{-1}, and k_{obsd} from 2.5 to 2.8 × 10^{-2} s^{-1}, nearly to humic acid model solution. Furthermore, the relationship between CdCC and dissolved organic carbon (DOC), nitrogen and sulfur contents of the water samples was discussed, and the influences from the anthropogenic activities around the sampling sites as well.

In Chapter Three, a softer competing ligand HMTP was used to simultaneously determinate Cd/CuCC of natural waters and the corresponding k_{obsd} of Cd/Cu complexes involved. The obtained extraction dynamic curve (-ln[ML] against t) shows a two-stage stepwise profile that reflected the competition of different ligands existing in the natural waters with HMTP toward Cd/Cu species, suggesting that there are different chemical forms of Cd/Cu in the natural waters. Through the comparison of Cd/CuCC of natural waters which are responsible to the different sampling location from Minjiang River, it was found that a significant correlation between Cd/CuCC and DOC in the water samples, and S/N content played an important role in regulating the self-purification capacity of the waters. On the other hand, the occurrences of the kinds of ligands in the natural waters are much influenced by anthropogenic activities.

In Chapter Four, considering the potential toxicity and inconvenience manipulation of dithizone and HMTP, a methylene monoamino diacritic acid chelating resin was used instead of the extracting ligands. Results indicated that the chelating resin is suitable for evaluating CdCC when moderate and strong organic ligands are existing in the water samples. It was successfully applied to the evaluation of the self-purification capacity of Furong Lake in the main campus of Xiamen University, and comparable to that of HMTP-based method. Synthesis of new type of chelating resin and design automatic device to be used for future automation of the CC and the corresponding k_{obsd} determination procedures should be

expected for more objective and efficient evaluation of the risk of heavy metal pollution in water system.

In Chapter Five, a summary of this thesis was concluded and the developing trend was also prospected.

Keywords: m**etal** complexing capacity; Dynamic method; complex lability; natural waters.

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